ISSN(Print) : 2320 -1967
ISSN(Online) : 2320 -1975

GLOBAL SCIENTIFIC INC.

ChemXpress

ORIGINAL ARTICLE

ChemXpress 8(2), 120-126, (2015)

Effect of grafting efficiency on dyeability of acrylic acid-g-cellulose fibre

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Abstract : Acrylic acid grafted cellulose fibre samples with graft efficiencies of 14, 18.3, 43.6, and 63.53% were dyed with basic, direct, and reactive dyes at neutral pH in the absence of electrolyte. Ungrafted cellulose fibre was also dyed to serve as control. Percentage exhaustion of the dyes by the samples as well as the amount of dye adsorbed per kilogram fibre were determined. In all cases, the higher the graft efficiency, the higher the amount of dye adsorbed. It was found that the samples adsorbed more malachite green, a basic dye, than the other dye classes used. © Global Scientific Inc.

Keywords : Dyeing; Graft efficiency; Basic dye; Direct dye; Reactive dye.

INTRODUCTION

The dyeing of cellulosic fibres are generally done with direct, vat, sulphur, azoic, and reactive dyes[11] although, in recent years, reactive dyes maintain the largest annual consumption in the world due to their brilliancy, variety of hue, high wet fastness and high applicability[9]. Dyeing with reactive and direct dyes requires the use of electrolytes and a high volume of water[9]. Although many different methods of waste water treatment have been used such as precipitation, ion-exchange, extraction, physico-chemical and biological treatments, most of these are inefficient because of their weak selectivity and/or high cost[3]. Basic dyes are known to have no affinity towards cotton fabrics. This drawback was overcome by the introduction of acidic groups into the polymer macro-molecules via radiation grafting in acrylic acid solution[5].

Grafting of vinyl monomers onto cellulose is an important tool for its modification and depending on the monomer grafted, the product gains new properties. Cellulose graft copolymer consists of side chains that are covalently bonded to the main polymer back-bone giving it a branched structure[7]. Grafted materials obtained from grafting vinyl monomers with functional groups such as acrylamide[2] and acrylic acid[6] onto cellulose have been used in the adsorption of hazardous contaminants such as heavy metal ions and dyes[4]. Graft copolymers are characterized by parameters such as percent polymerization, graft percent, water absorption capacity, and graft efficiency. Graft efficiency shows the fraction of monomer grafted onto cellulose among the amount of monomer converted to graft polymer plus the homopolymer, in other words, it is the fraction of polymer which is grafted to cellulose in total polymer[7].

In the present work, acrylic acid grafted cellulose fibre samples of various graft efficiencies were dyed with basic, direct and reactive dyes under neutral pH in the absence of electrolyte.

MATERIALS AND METHODS

Materials and analytical equipment

Acrylic acid grafted cellulose fibres with varying graft efficiencies were prepared by Abdullahi (2014). The bleached cotton fibre used in this study was an original sample used for grafting and was obtained from the Institute of Agricultural Research (IAR), Ahmadu Bello University, Zaria, Nigeria.

Chemicals/reagents

All chemicals were of reagent grade and were used without further purification. The dyes used were Malachite Green and Methylene Blue (basic dyes), Solophenyl Yellow PFL and Cuprophenyl Brilliant Blue 2BL (direct dyes), Tectilon Blue 4G and Tectilon Yellow 2G (reactive dyes).

Analytical equipment

Jenway UV/Visible spectrophotometer (6405) was used in Multiuser Laboratory, Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria. A&D electronic weighing balance, Gallenkamp thermostatic water bath (made in England), and IKA WERKE mechanical shaker (made in England) were used in the Department of Textile Science and Technology, Ahmadu Bello University, Zaria, Nigeria.

Methods

Dyeing of the samples

Bleached cellulose fibre (sample E), 0.1g, was added to 5ml of 0.5% Malachite Green dye solution in 25ml test tube and the solution made up to 10ml with distilled water (goods to liquor ratio, 1:100). The test tube was placed in a 250ml beaker contained in a thermostatic water bath. The sample was agitated by placing the water bath on a mechanical shaker at 100 revolutions /minute and the dyeing carried out at 40^{o}C for 24 hours. The same procedure was repeated using 1% Methylene Blue, Solophenyl Yellow PFL, Cuprophenyl Brilliant Blue 2BL, Tectilon Blue 4G, and Tectilon Yellow 2G for the grafted samples with graft efficiencies of 14, 18.3, 43.6, and 63.53% (samples A, B, C, and D respectively).

After dyeing, the samples were squeezed and the concentration of the residual solution determined by the absorbance at 615nm for Malachite Green, 665nm for Methylene Blue, 405nm for Solyphenyl Yellow PFL, 590nm for Cuprophenyl Brilliant Blue 2BL, 615nm for Tectilon Blue 4G, and 415nm for Tectilon Yellow 2G.

Determination of % exhaustion

The uptake of the dyes by the ungrafted cellulose fibre and the grafted samples were measured in each case by sampling the dye bath before dyeing and after dyeing on a UV/Visible spectrophotometer and using calibration curves to determine the % concentration of the residual dye solution after dyeing. The percentage of dye bath exhaustion (%E) was calculated using the relation:

$$\%E = \frac{C1-C2}{C1}(100) \quad 2.1$$

where *C1*= % concentration before dyeing, and *C2*= % concentration after dyeing.

Determination of the amount of dye adsorbed per kg fibre

The amount of dye adsorbed by the ungrafted cellulose fibre and grafted samples were determined by the relation:

$$g\ dye\ per\ kg\ fibre = (0.5E)(100) \quad 2.2$$

where E= % exhaustion.

RESULTS AND DISCUSSION

Calibration curves

Figure 1 showed the calibration curves for the dyes used where the plots have a linear relationship starting from the origin. They obey Beer-Lambert's law and in all cases, the correlation coefficient value is greater than 98% which is statistically acceptable.

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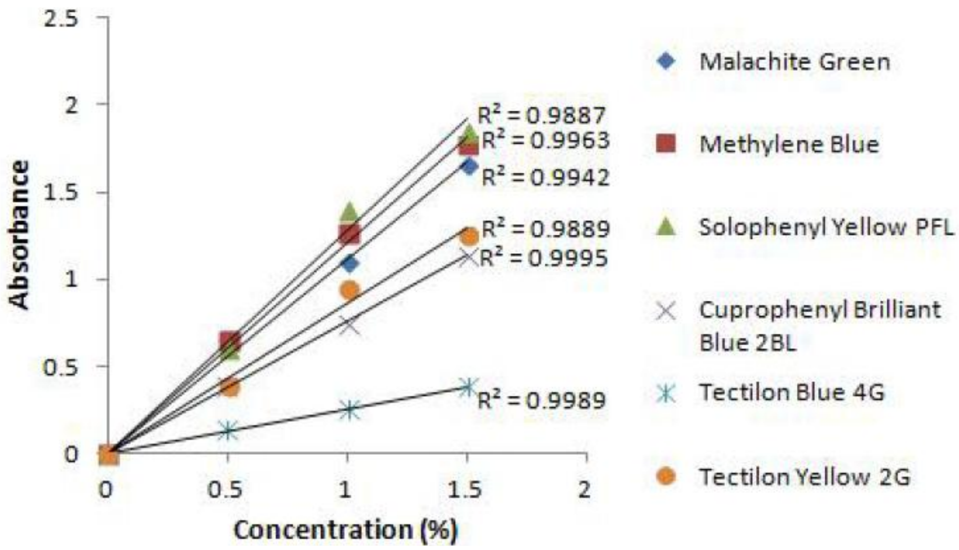
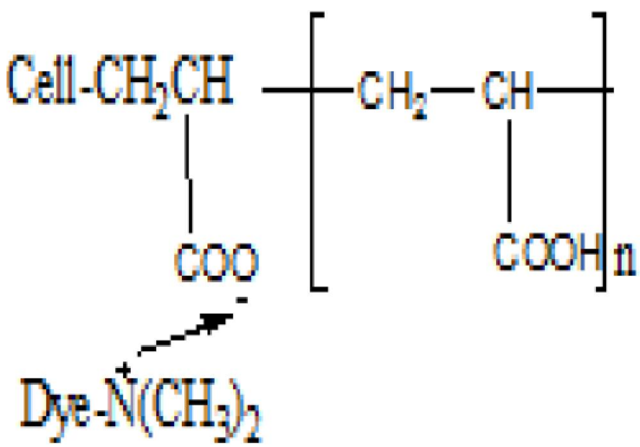


Figure 1 : Calibration curves for the dyes used



Scheme 1 : Mechanism for the adsorption of basic dyes by the grafted samples

Adsorption of basic dyes

Figure 2 shows that sample D adsorbed more Malachite Green than any other dye class used in the study. The Sample adsorbed about 500g dye above the ungrafted cellulose fibre (sample E), and almost, twice higher than sample A.

The most probable mechanism is ion-exchange between the dye cation and an anion from the free carboxylic acid groups on the grafted cellulose surface. The higher the grafting efficiency, the higher the number of carboxylate anions for ion-exchange and hence a higher adsorption capacity. A π-π dispersive interaction between the dye and the fibre

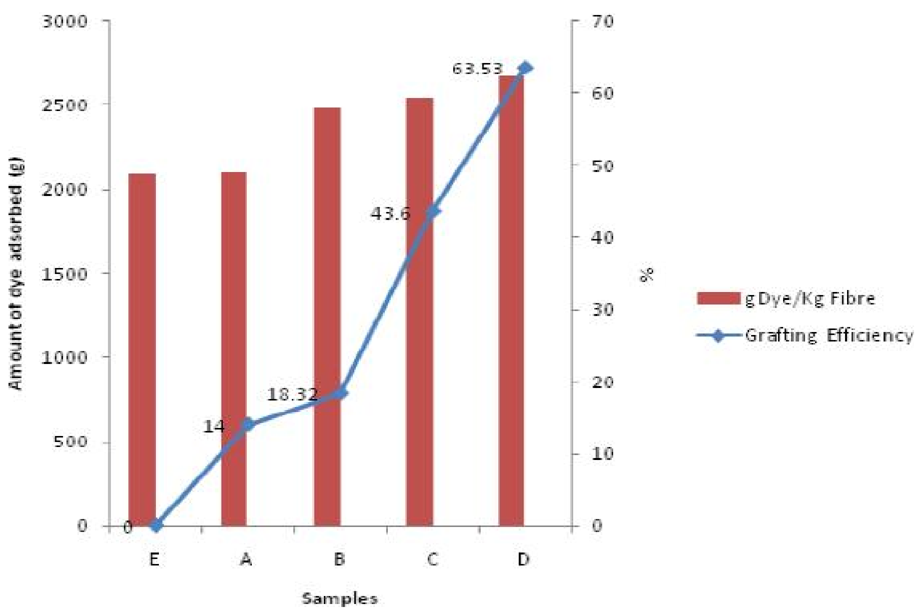


Figure 2 : Effect of grafting efficiency on the adsorption of malachite green

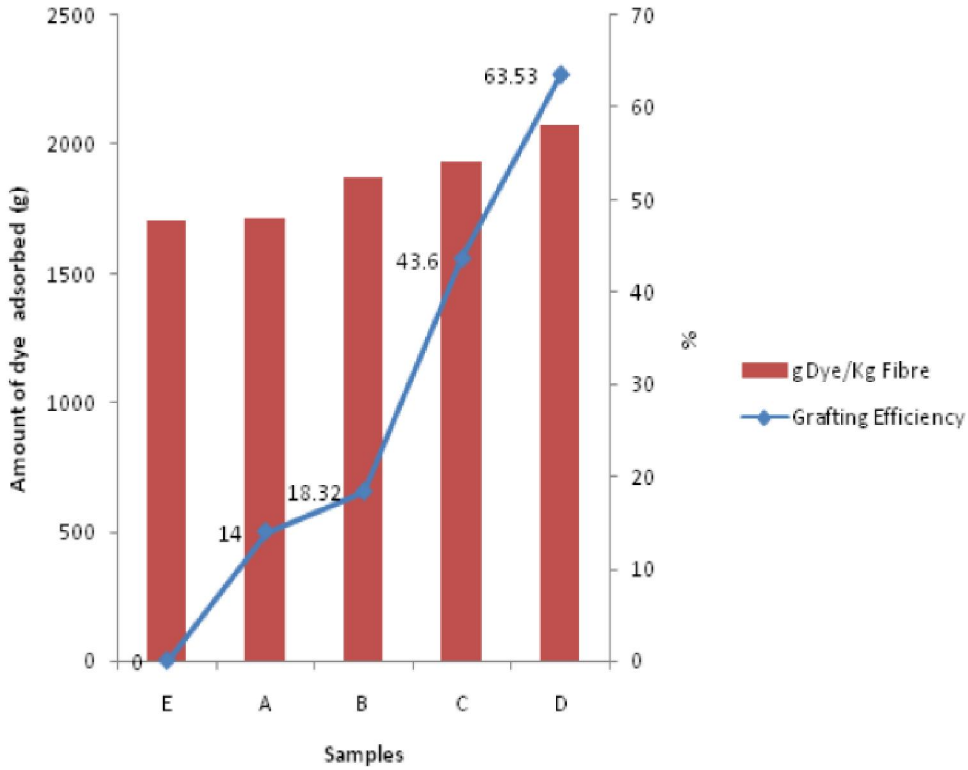
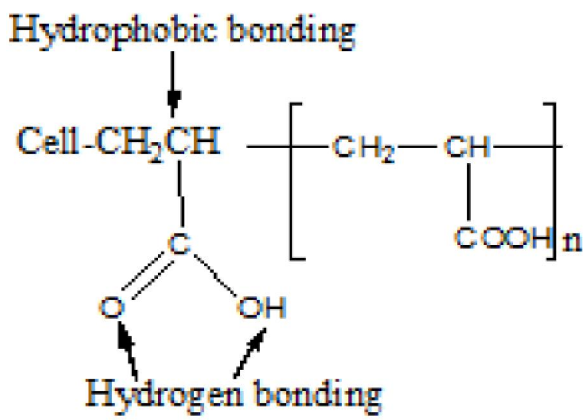


Figure 3 : Effect of grafting efficiency on the adsorption of methylene blue



Scheme 2 : Mechanism for the adsorption of direct dyes by the grafted samples

could have also contributed to adsorption.

Although Malachite Green and Methylene Blue might have the same adsorption mechanism, sample D adsorbed about 600g more of the former than the latter. This could be due to the fact that Malachite Green is more planar and bulkier than Methylene Blue and hence greater affinity for the grafted samples. Figure 3 shows the effect of grafting efficiency on Methylene Blue adsorption while Scheme 1 shows mechanism for adsorption of basic dyes.

Adsorption of direct dyes

It can be seen that the adsorption of Cuprophenyl Brilliant Blue 2BL by an ungrafted sample (sample E) was higher than that of Solophenyl Yellow PFL dyed sample A, but sample D adsorbed more of the latter than the former. Sample D adsorbed about 1000g dye more than the ungrafted sample (sample E) for both Solophenyl Yellow and Cuprophenyl Brilliant Blue as shown in Figures 4 and 5 respectively.

All water soluble dyes are electrolytes, and in aqueous solution, dissociate into the dye ion and the colourless compensating ions having an opposite charge to that of the former. The coloured ion of direct dyes is negatively charged and the grafted sample, when immersed in dye solution, due to the presence of free carboxylic acid groups, becomes negatively charged. Repulsive forces eventually develop but the dyes might contain some impurities which could overcome some of the potential barriers, allowing certain amount of dye to be adsorbed[8]. The adsorption could also be enhanced by the fact that swollen hydrogels have a high water absorption capacity and therefore the dye in solution would

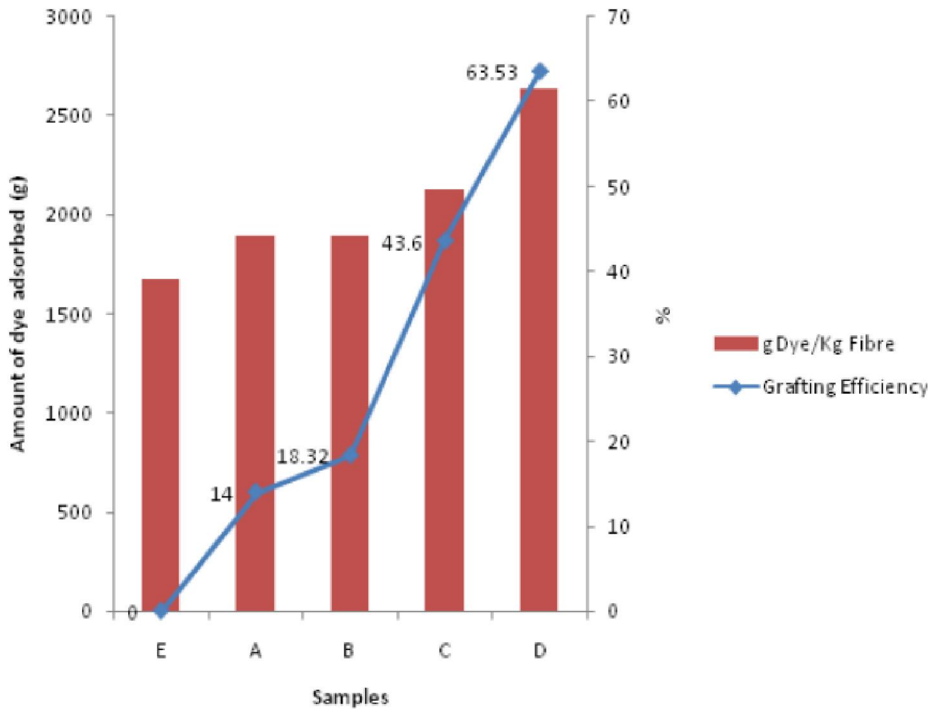


Figure 4 : Effect of grafting efficiency on the adsorption of solophenyl yellow PFL

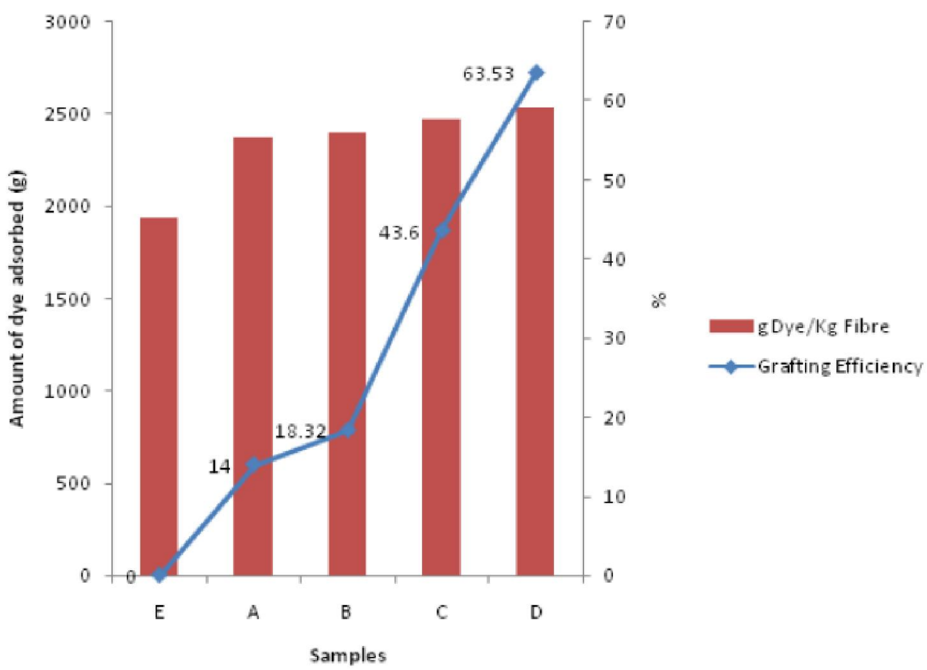


Figure 5 : Effect of grafting efficiency on the adsorption of cuprophenyl brilliant blue 2BL

interact more with the grafted samples.

Due to large molecular size of direct dyes, Van der Waals' attractions could be a possible reason for significant dye adsorption. Moreover, since the grafted samples have a very high water absorption capacity and also contain several methyl groups available for hydrophobic bonding and carboxyl groups for inter and intra-molecular hydrogen bonding with suitable groups in the dye, adsorption could be enhanced with increasing graft efficiency. Due to a large number of methyl groups on the surface of the grafted samples, they are more hydrophobic in nature and therefore the major reason for significant dye adsorption could be hydrophobic bonding as

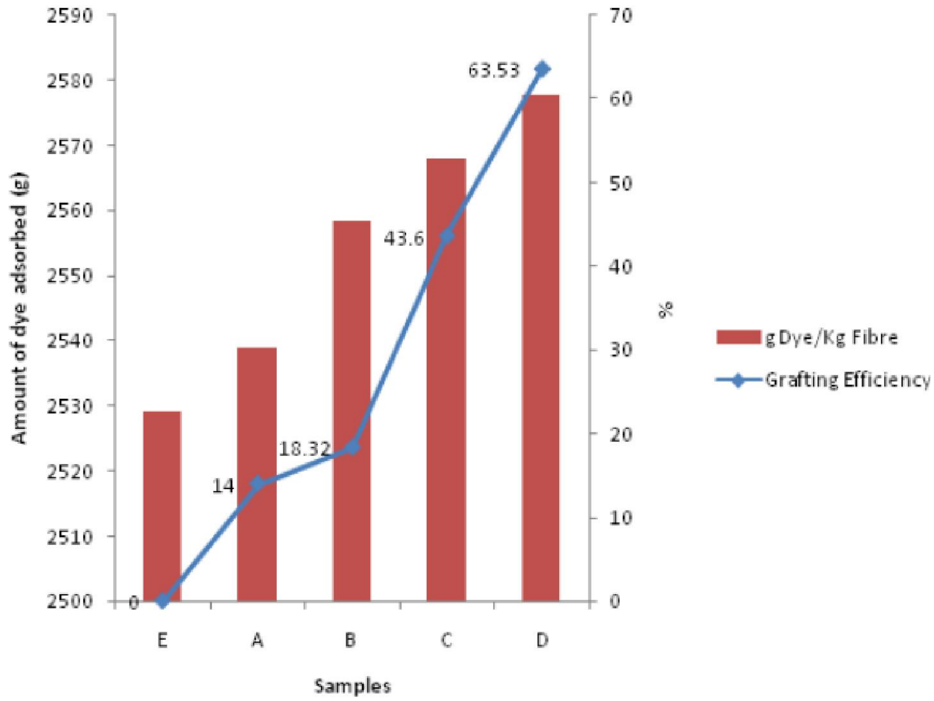


Figure 6 : Effect of grafting efficiency on the adsorption of tectilon blue 4G

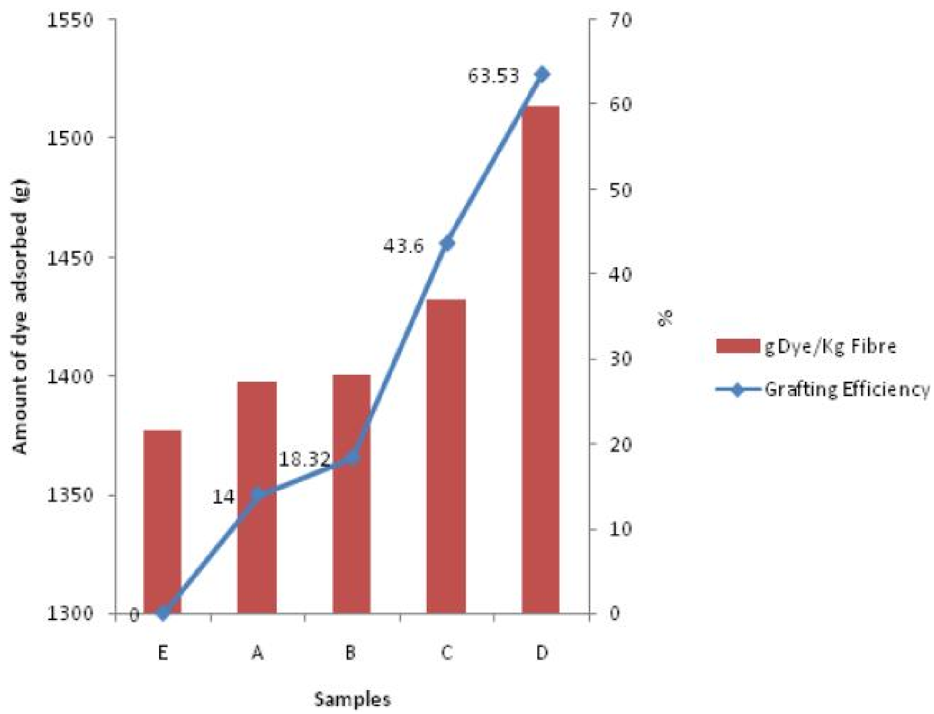


Figure 7 : Effect of grafting efficiency on the adsorption of tectilon yellow 2G

shown in Scheme 2.

Adsorption of reactive dyes

Figures 6 and 7 show the effect of graft efficiency on the adsorption of Tectilon Blue 4G and Tectilon Yellow 2G respectively, where about 1000g of the former was adsorbed above the latter for both ungrafted cellulose fibre and the grafted samples. The difference in adsorption between the ungrafted and the grafted samples was not significant which could be due to the fact that the major possible adsorption mechanism is the weak ë−ë dispersive interactions between the dye and the fibre[10]. Like di-

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rect dyes, reactive dyes are electrolytes and hence the same adsorption mechanism could be operative.

CONCLUSION

For all the dye classes used, Sample D, with a grafting efficiency of 63.53%, had the highest adsorption (gram dye/ kilogram fibre), while the ungrafted cellulose fibre had the lowest adsorption values. Grafting of cellulose with acrylic acid enhances the possibility of dyeing cellulosic fibres at neutral pH with reactive and direct dyes in the absence of electrolyte. Even though basic dyes have no affinity for cellulose, the grafted samples, due to the presence of carboxylic acid groups, adsorbed large amount of Malachite Green up to 2678.17g/kg fibre which was the highest adsorption value compared to other dye classes.

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